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SUPPORT EFFECT IN THE THERMAL DECOMPOSITION OF SOME CATALYST PRECURSORS

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Abstract

The thermal decompositions of ammonium metavanadate, molybdic acid and ammonium phosphomolybdate supported on carborundum or silica were subjected to non-isothermal kinetic study. The compensation effect is discussed in connection with the quantitative estimation of the support effect.

Keywords: compensation effect, isokinetic temperature, non-isothermal kinetics, support effect, supported precursors

Introduction

In order to obtain supported catalysts, the thermal decomposition of the precursor on the support is a compulsory step. The thermal stability of any compounds varies to a rather significant extent on change from the pure bulk to a supported state; depending on the magnitude of this variation, a support is characterized as 'inert' or 'active'. A knowledge of the thermal behaviour of precursor/support systems is of great importance for the development of industrial catalysts.

Use of the methods of non-isothermal kinetics [1] to investigate the thermal behaviour of precursor/support systems indicates that the currently observed compensation effect [2] can be regarded as a support effect [3, 4].

The aim of the present paper was to study the support effects of carborundum (C) and silica (S) in the thermal decompositions of ammonium metavanadate (V), molybdic acid (A) and ammonium phosphomolybdate (P).

Experimental

Details on the prepared samples, with different concentrations of supported substance, are presented in Table 1. In order to avoid the effects of thermal gradients, comparative samples of mechanical mixtures with the same concentration were prepared.

The thermal curves were recorded with a Q Derivatograph (MOM, Budapest) in static air atmosphere with the corresponding support as reference compound in a platinum crucible; the heating rate was 10 K min^{-1} in the range 300–1200 K.

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Table 1 Characteristics of the studied samples

Symbol	Support	Type of sample	Conc./m%	Symbol	Support	Type of sample	Conc./m%
			Ammonium metavanadate				
VCM10			10	VCS10			10
VCM15			15	VCS15			15
VCM20	SiC	mixed	20	VCS20	SiC	supported	20
VCM30			30	VCS30			30
VCM40			40	VCS40			40
VSM10			10	VSS10			10
VSM15			15	VSS15			15
VSM20	SiO_2	mixed	20	VSS20	SiO_2	supported	20
VSM30			30	VSS30			30
VSM40			40	VSS40			40
			Molybdic acid				
MCM10			10	MCS10			10
MCM15			15	MCS15			15
MCM20	SiC	mixed	20	MCS20	SiC	supported	20
MCM25			25	MCS25			25
MCM30			30	MCS30			30
MSM10			10	MSS10			10
MSM15			15	MSS15			15
MSM20	SiO_2	mixed	20	MSS20	SiO_2	supported	20
MSM25			25	MSS25			25
MSM30			30	MSS30			30
			Ammonium phosphomolybdate				
PCM10			10	PCS10			10
PCM15			15	PCS15			15
PCM20	SiC	mixed	20	PCS20	SiC	supported	20
PCM25			25	PCS25			25
PCM30			30	PCS30			30
PSM10			10	PSS10			10
PSM15			15	PSS15			15
PSM20	SiO_2	mixed	20	PSS20	SiO_2	supported	20
PSM25			25	PSS25			25
PSM30			30	PSS30			30

The derivatograph was coupled to a PC, a special program being used for the acquisition and processing of the experimental data.

Results and discussion

The kinetic parameters presented in Table 2 were evaluated by the Popescu-Segal method [5, 6], using the Flynn-Wall-Ozawa equation. The validity of the method applied and the accuracy of the results are indicated by simulation of the TG curves, as given in Fig. 1.

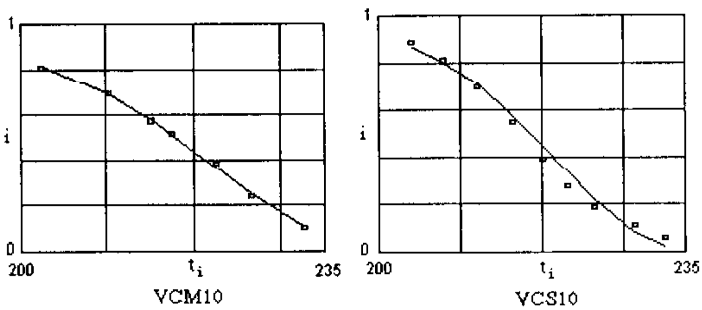


Fig. 1 Simulated x *vs.* t (°C) curves and the experimental points (□); $x=1-\alpha$, where is the corresponding value of conversion

Support effect

The values of E and ln$A$ (Table 2) exhibit an obvious linear dependence for the same precursor/support pairs at different concentrations (Fig. 2). This compensation effect is expressed by

$$\ln A = bE + c \tag{1}$$

The slope b corresponds to the isokinetic temperature Θ:

$$b = (R\Theta)^{-1} \tag{2}$$

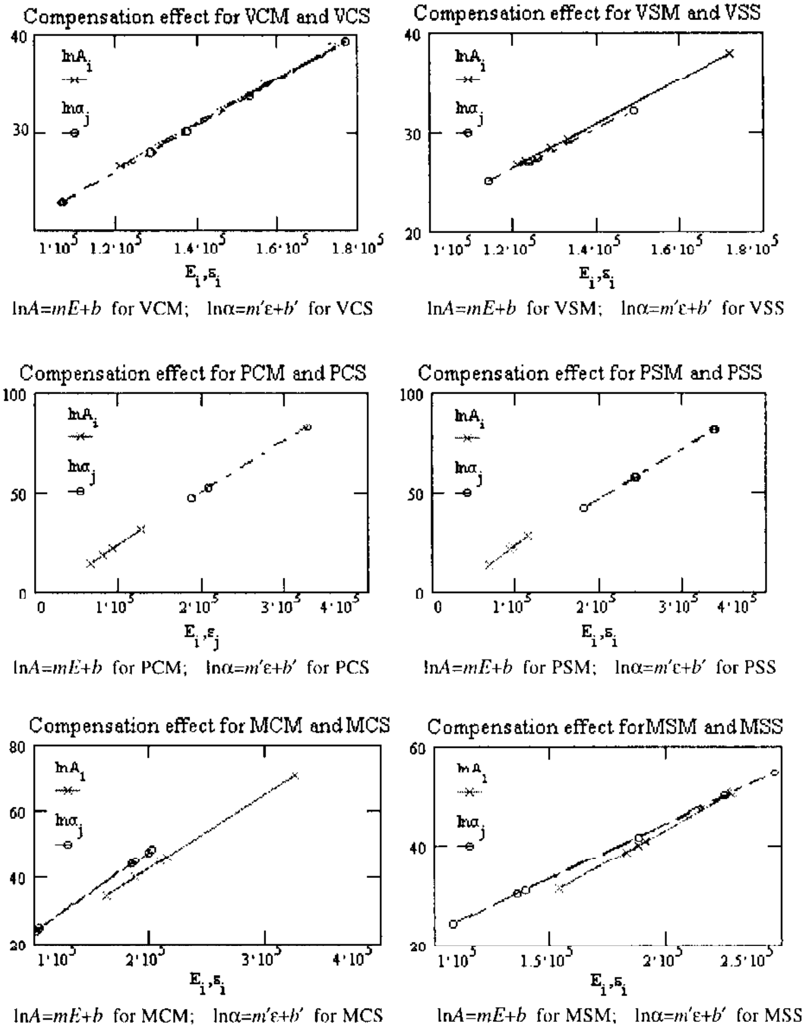
which is thought to be a certain decomposition temperature [7]. The data are systematized in Table 3.

The difference between Θ_{sup} (for the supported precursor) and the corresponding Θ_{mix} (for the mechanical mixture) is a parameter suggested as an indicator of the magnitude of the support effect. Indeed, for metavanadate on carborundum, a difference of 8 K is rather negligible, but a $\Delta\Theta$ higher than 40–80 K is evidence of a support effect.

Unexpectedly high $\Delta\Theta$ values for molybdic acid and ammonium phosphomolybdate on carborundum demonstrate a certain influence of SiC as support, but in any case it is smaller than that of SiO_2.

Table 2 Kinetic parameters from the Flynn-Wall-Ozawa equation: $\ln F = -1/RT + \ln(A/a) + \ln(E/R) - 5.33$

Sample	E_a/ J mol$^{-1}\cdot 10^{-5}$	ln*A*	*n*	Sample	E_a/ J mol$^{-1}\cdot 10^{-5}$	ln*A*	*n*
VCM10	1.53	34.98	0.9	VCS10	1.07	23.04	0.9
VCM15	1.57	34.99	0.9	VCS15	1.53	33.75	0.9
VCM20	1.74	37.95	0.9	VCS20	1.77	38.99	0.9
VCM30	1.41	30.55	0.9	VCS30	1.38	29.47	0.9
VCM40	1.21	26.30	0.9	VCS40	1.29	28.03	0.9
VSM10	1.29	29.23	0.9	VSS10	1.14	24.79	0.9
VSM15	1.72	37.75	0.9	VSS15	1.14	25.36	0.9
VSM20	1.33	38.99	0.9	VSS20	1.26	27.84	0.9
VSM30	1.21	29.47	0.9	VSS30	1.24	26.91	0.9
VSM40	1.23	28.03	0.9	VSS40	1.49	30.33	0.9
MCM10	3.25	69.83	1.7	MCS10	1.01	22.15	1.5
MCM15	2.09	49.02	1.7	MCS15	1.85	42.59	1.5
MCM20	1.62	32.52	1.7	MCS20	2.21	50.23	1.5
MCM25	2.15	44.65	1.7	MCS25	1.99	52.94	1.5
MCM30	1.63	36.41	1.7	MCS30	1.05	27.83	1.5
MSM10	2.29	52.77	1.7	MSS10	2.25	53.36	2.9
MSM15	1.83	40.06	1.7	MSS15	1.36	32.29	2.9
MSM20	1.91	39.74	1.7	MSS20	1.08	23.96	2.9
MSM25	1.54	31.99	1.7	MSS25	2.47	53.52	2.9
MSM30	2.28	49.15	1.7	MSS30	1.40	31.11	2.9
PCM10	3.25	69.835	0.9	PCS10	1.01	22.15	0.9
PCM15	2.09	49.02	0.9	PCS15	1.85	42.59	0.9
PCM20	1.62	32.52	0.9	PCS20	2.21	50.23	0.9
PCM25	2.15	44.65	0.9	PCS25	1.99	52.94	0.9
PCM30	1.63	36.41	0.9	PCS30	1.05	27.83	0.9
PSM10	2.29	52.77	0.9	PSS10	2.25	53.36	1.3
PSM15	1.83	40.06	0.9	PSS15	1.36	32.29	1.3
PSM20	1.91	39.74	0.9	PSS20	1.08	23.96	1.3
PSM25	1.54	31.99	0.9	PSS25	2.47	53.52	1.3
PSM30	2.28	49.15	0.9	PSS30	1.40	31.11	1.3



ln$A$=mE+b for VCM; lnα=m'ε+b' for VCS

ln$A$=mE+b for VSM; lnα=m'ε+b' for VSS

ln$A$=mE+b for PCM; lnα=m'ε+b' for PCS

ln$A$=mE+b for PSM; lnα=m'ε+b' for PSS

ln$A$=mE+b for MCM; lnα=m'ε+b' for MCS

ln$A$=mE+b for MSM; lnα=m'ε+b' for MSS

Fig. 2 Diagrams of the compensation effect

Conclusions

1. The thermal behaviour of ammonium metavanadate, molybdic acid and ammonium phosphomolybdate supported on carborundum or on silica was investigated.

2. The non-isothermal kinetic parameters determined at different precursor concentrations reveal a compensation effect, considered to be a support effect.

3. The difference between the isokinetic temperatures of the supported and the mixed sample is suggested as an indicator of the magnitude of the support effect.

4. Carborundum exerts an obviously smaller effect than that of silica on the thermal decomposition of the supported precursor.

Table 3 Isokinetic temperature Θ

Support	Sample	Θ/K	Effect of deposition $\Delta\Theta=\Theta_{sup}-\Theta_{mixt}$
SiC	VCM	522	−8
	VCS	514	
SiO_2	VSM	544	+43
	VSS	587	
SiC	MCM	435	43
	MCS	478	
SiO_2	MSM	402.9	89.5
	MSS	492.4	
SiC	PCM	548.5	−51.2
	PCS	497.3	
SiO_2	PSM	463.7	88.1
	PSS	551.8	

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